TRANSFERENCE STUDIES ON POLYELECTROLYTES

BY

JOHN JERRY ONDREJCIN

S.B., University of Chicago, 1944
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

URBANA, ILLINOIS

1950

TRANSFERENCE STUDIES ON POLYELECTROLYTES

BY

JOHN JERRY ONDREJCIN

S.B., University of Chicago, 1944
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

URBANA, ILLINOIS

1950

ACKNOWLEDGMENT

The author wishes to express his gratitude to Professor F. T. Wall for his guidance and many helpful suggestions throughout the course of this problem. He is also indebted to Miss Marika Pikramenou for her assistance with the experimental work.

The funds making this investigation possible were furnished by the Office of Rubber Reserve, Reconstruction Finance Corporation, and by the Firestone Tire and Rubber Company.

R. UNIV.
BIBLIOTHEEK
LEIDEN

TRANSFERENCE STUDIES ON POLYELECTROLYTES

Introduction

Polyelectrolytes or polymers capable of ionization when dissolved in some polar solvent have been the subject of a considerable number of investigations in recent years. Perhaps the best known class of polyelectrolytes are the proteins which, although studied most extensively, are difficult to treat except from an empirical standpoint because of their molecular complexity.

As a simple model to explain anomalous protein behavior Staundinger and Tromsdorf (1,2) chose polyacrylic acid and studied the properties of its aqueous solutions. Other examples of typical electrolytes are the hydrolyzed copolymer of maleic acid anhydride and styrene, polyvinyl amine, and polyvinylpyridine in acid solutions.

The polymeric ions formed upon solution of these substances are capable of acquiring a large number of positive or negative charges. The resulting electrostatic forces tend to change the molecular configuration as the degree of ionization varies and these changes are reflected in the macroscopic properties of aqueous polyelectrolyte solutions. In contrast to ordinary weak electrolytes, polyelectrolytes do not follow Ostwald's dilution law. Ordinary polymers like polystyrene dissolve in homopolar solvents giving solutions which have unusual properties. Their behavior, unlike polyelectrolytes, is not complicated by ionization.

Since the early work in polyelectrolytes, osmotic pressure, viscosity, light scattering, conductance (3), diffusion (4), and electrolytic transference measurements have been the experimental means used in an attempt to gain a fundamental understanding of the nature of the phenomena exhibited by these unusual solutions.

Discussion Of Results

Poly-2-vinylpyridine was prepared from the monomer using Redox techniques. The purified product was dissolved in hydroiodic acid solutions at various concentrations and degrees of neutralization.

These solutions were electrolyzed in a cell separated into anode and cathode compartments by a coarse sintered glass frit. A coil of platinum wire served as the anode and the cathode was a silver-silver iodide electrode. Conductance measurements were carried out using an alternating current type of Wheatstone bridge and an audio-frequency oscillator. Hydrogen ion concentrations were determined with a Beckmann pH meter. Iodine ^{131}, a radioactive isotope of iodine,was added as a tracer to the initial solutions so that the distribution of the iodide ion in the solution compartments at the completion of an experiment could be calculated by use of the data obtained with a Geiger counter.

With these experimentally determined quantities it is possible from theoretical considerations to calculate the transference number of the polycation from the following expression

$$t_+ = (K - K_{OH} - K_H)/K \quad — \quad \Lambda_I rf/1000K$$

where K, K_{OH}, K_H, are the specific conductances of the solution (corrected for the solvent), the hydroxyl ion, and the hydrogen ion respectively, Λ_I the equivalent conductance of the iodide ion, r the equivalents of acid added, and f the fraction of iodide ions free in solution. The transference number of the polymer ion varied between 0.1 and 0.2 decreasing slightly with an increase in the degree of neutralization.

Other related quantities investigated and calculated included the variation of pH with the degree of neutralization and concentration, the fraction of the polymer ion charged, the number of iodide ions bound to the polyion, the rational mobility, and the equivalent conductance of the poly-2-vinylpyridonium cation.

BIBLIOGRAPHY

(1) Staudinger, "Die Hochmolekulararen Organischen Verbindungen", Julius Springer, Berlin (1932)

(2) Trommsdorf, Doctoral Dissertation, Freiburg (1931)

(3) Fuoss, R. M., and Strauss, U. P., J. Polmer Sci., 3, 246 (1948)

(4) Huizenga, J. R., "A Study of the Transference Properties of Polymeric Electrolytes using Radioactive Tracers", Thesis, Univ. of Illinois (1949

(5) Korff, S. A., "Electron and Nuclear Counters", D. Van Nostrand Co., Inc. New York (1946)

VITA

The author was born in Chicago, Illinois on July 20, 1921. He attended a local elementary school and was graduated from Foreman High School in January, 1939. That year he enrolled in Wright Junior College in Chicago graduating in 1941. His studies at the University of Chicago were interrupted when he enlisted in the Signal Corps in July, 1942, serving with the Armed Forces until discharge as a Second Lieutenant in the Infrantry in April, 1946. The Bachelor of Science degree from the University of Chicago was awarded him in absentia in 1944. In February, 1947, he enrolled in the Graduate College of the University of Illinois. He was employed as a special research assistant under contract with the Rubber Reserve Corporation from February, 1948, to September, 1949, and held the Firestone Tire and Rubber Company fellowship from September, 1949, to June, 1950.

The author is a member of Sigma Xi, Phi Lambda Upsilon, and Alpha Chi Sigma.